

AD-A144 646

HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC STUDIES OF THE
ION EXCHANGE SELEC. (U) TEXAS A AND M UNIV COLLEGE
STATION DEPT OF CHEMISTRY R B MOORE ET AL. 86 AUG 84

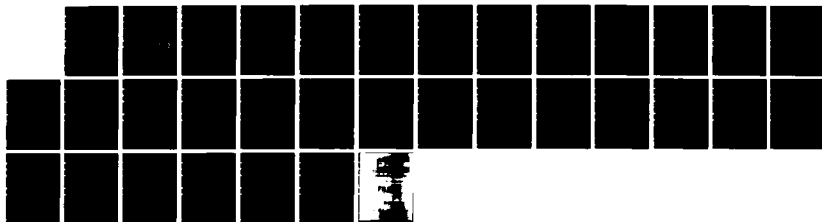
1/1

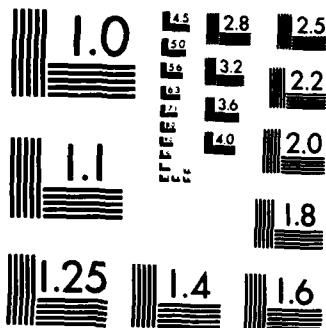
UNCLASSIFIED

N00014-82-K-0612

F/G 7/4

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

Task No. NR 627-838

TECHNICAL REPORT NO. 6

12

High Performance Liquid Chromatographic Studies of the Ion Exchange
Selectivity of Nafion

by

Robert B. Moore, III, James E. Wilkerson and Charles R. Martin

Prepared for Publication

in

Analytical Chemistry

Department of Chemistry
Texas A&M University
College Station, Texas 77843

August 6, 1984

DTIC
ELECTE

AUG 16 1984

B

Reproduction in whole or in part is permitted for
any purpose of the United States Government

* This document has been approved for public release
and sale; its distribution is unlimited

* This statement should also appear in Item 10 of Document Control Data
- DD Form 1473. Copies of form available from cognizant contract
administrator.

84 08 13 003

AD-A144 646

DTIC FILE COPY

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #6	2. GOVT ACCESSION NO. AD-A144646	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC STUDIES OF THE ION EXCHANGE SELECTIVITY OF NAFION		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert B. Moore, III, James E. Wilkerson and Charles R. Martin		8. CONTRACT OR GRANT NUMBER(s) N00014-82K-0612
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Texas A&M University College Station, Texas 77843		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 627-838
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217		12. REPORT DATE August 6, 1984
		13. NUMBER OF PAGES 23
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Presented at the Pittsburgh Conference, March, 1984		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Nafion, Ion Exchange Selectivity, Ion Exchange Membranes, Ionomers		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Nafion films were coated on 5 μ m octadecyl-derivatized silica. HPLC columns were packed with this film-modified ODS and the ion exchange selectivity of Nafion was studied. A homologous series of organic cations was used to probe the ion exchange properties of Nafion. These studies show that Nafion has remarkable affinity for hydrophobic cations. The logs of the ion exchange selectivity coefficients for the cations of the homologous series were found to increase in a linear fashion with the molecular weight of the cation.		

DD FORM 1473
1 JAN 73EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT

The theoretical and practical implications of this unusual ion exchange selectivity are discussed.



Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

High Performance Liquid Chromatographic Studies
of the Ion Exchange Selectivity of Nafion

Robert B. Moore, III, James E. Wilkerson
and Charles R. Martin*

Department of Chemistry
Texas A&M University
College Station, Texas 77843

Brief

Nafion-based HPLC columns were prepared by coating 5 μ M ODS with Nafion films. Studies of the ion exchange selectivity of these columns showed that Nafion has remarkable affinity for hydrophobic cations.

Abstract

Nafion films were coated on 5 μ M octadecyl-derivatized silica. HPLC columns were packed with this film-modified ODS and the ion exchange selectivity of Nafion was studied. A homologous series of organic cations was used to probe the ion exchange properties of Nafion. These studies show that Nafion has remarkable affinity for hydrophobic cations. The logs of the ion exchange selectivity coefficients for the cations of the homologous series were found to increase in a linear fashion with the molecular weight of the cation. The theoretical and practical implications of this unusual ion exchange selectivity are discussed.

INTRODUCTION

We have recently reported results of fundamental studies of ion exchange reactions involving hydrophobic cations in Nafion films at electrode surfaces (1). These studies have shown that Nafion has remarkable affinity for such cations. For example, the selectivity coefficient associated with the exchange of Na^+ with $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine) in Nafion was found to be 5.7×10^6 (1). While these and other studies (2-6) clearly show that hydrophobic interactions can play a role in determining the strength of the Nafion/counterion interaction, structural and charge differences in the counterions used made quantitative conclusions about the contribution of the hydrophobic effect difficult. Furthermore, the electrochemical isotherm method used (1,7) is extremely tedious and time consuming.

We are interested in learning more about the contribution of the hydrophobic effect to counterion binding in Nafion and other ionomers (8). It seemed likely that high performance liquid chromatography (HPLC) would prove to be a much more convenient and powerful tool for studying ion exchange reactions in these polymers. To test this hypotheses, we have used an HPLC method to study ion exchange reactions of a homologous series of alkylpyridinium ions in Nafion. We report results of these and related studies here.

EXPERIMENTAL SECTION

Apparatus. The liquid chromatograph consisted of a Spectra-Physics 8700 solvent delivery system, a Rheodyne model 7125 injection valve with a 10- μL sample loop, a Gilson HoloChrome HM/HPLC UV/Visible detector, and a Linear Instruments model 500 laboratory chart recorder. The 15 cm x 4.6 mm (i.d.)

stainless steel columns (Rainin) were packed using a Haskel air driven fluid pump. The polymer was dissolved in a Parr model 4562 "Mini" Pressure Reactor.

Reagents. Tetramethylammonium bromide (TMAB) (Aldrich) was recrystallized from ethanol and water. Methylviologen (MV^{2+}) was obtained from Aldrich Chemical Co. Water was obtained from a Milli-Q water purification system, and methanol was MCB Omnisolv. The Nafion (1100 equivalent weight, EW) was obtained from E.I. du Pont de Nemours and Co. A homologous series of organic cations was prepared by allowing pyridine (Fisher Scientific Co.) to react with various linear alkyl bromides (1-bromoethane to 1-bromopentane) (Aldrich), at room temperature, for 5 days. The products were then recrystallized from an ethanol-ether solution. All other reagents were of the highest quality available and were used without further purification.

Preparation of Chromatographic Columns. A stock solution of the Nafion polymer was prepared using the procedure of Martin et al. (9). The concentration of this solution (0.34 (w/v) %) was determined by evaporating a known volume to dryness, in vacuo, and weighing the residue. A 0.01% solution was prepared from this stock solution by diluting with 50:50 ethanol-water. Octadecyl-derivatized silica (ODS) (5 μ M average diameter) and underivatized silica (Nucleosil 100-10) were obtained from Rainin. We initially attempted to coat the underivatized silica but found that Nafion would not adhere. We believe that this is because both Nafion and silica are anionic (and, therefore, electrostatically repellant) and because Nafion is hydrophobic while silica is hydrophilic. This latter point is strengthened by our observation that Nafion will not stick to glass but sticks quite nicely to dimethyldichlorosilane treated glass (10). It is of interest to note

that Kirkland has succeeded in getting a lower EW Nafion to stick to silica (11,12).

Nafion's preference for hydrophobic surfaces is further demonstrated by the fact that it will adhere to ODS; therefore, ODS was used as the substrate material. 2.5 g of 5 μ M ODS were added to 25 mL of the 0.01% Nafion solution. The solvent was evaporated from the resulting slurry by stirring in a water bath at 70°C. The modified ODS was then transferred to a vacuum oven and stored overnight at 70°C.

The quantity of Nafion on the packing material was measured using the following procedure. After packing, the column was rinsed with 200 mL of triply distilled water (flow rate = 1 mL min⁻¹). The -SO₃⁻ sites were then quantitatively converted to the ethylpyridinium salt form by passing a large volume of a 10⁻³ M aqueous solution through the column. The column was rinsed with water until all excess ethylpyridinium was removed (absorbance returned to baseline). The ionically bound ethylpyridinium was then quantitatively eluted from the column with 0.1 TMABr in methanol. The eluant was collected, and the concentration of ethylpyridinium determined spectrophotometrically. The volume of Nafion on the ODS (the volume of the stationary phase, V_s) was calculated by multiplying the moles of sulfonate sites by the equivalent weight and dividing by the density of the Nafion (5).

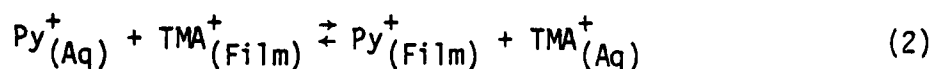
Prior to packing, both the ODS and ODS-Nafion particles were sized by adding them to 100 mls of methanol, agitating, allowing time for the majority of the particles to settle, and then drawing off the methanol, which contained fines. This process was repeated until the methanol remained relatively clear after sedimentation. Both ODS and ODS-Nafion columns were packed using the down-flow method of high pressure slurry-packing (13).

Chromatographic Conditions and Procedures. The various mobile phases were prepared by programming the Spectraphysics 8700 to mix appropriate quantities of either pure water or pure methanol with a solution of the desired salt (e.g., NaBr, TMABr, etc.). All mobile phase solvents were passed through a 0.2 μ M nylon filter (Rainin), and degassed with helium prior to use. All chromatographic experiments were carried out at a flow rate of 1 mL/min, except during studies of efficiency as a function of flow rate. The columns were operated at ambient temperature ($22 \pm 1^\circ\text{C}$) and the detector was operated at 254 nm. Column void volumes were determined using concentrated aqueous NaNO_3 solutions (14).

The retention characteristics of the Nafion columns were evaluated using the series of alkylpyridinium cations as probes. The Nafion $-\text{SO}_3^-$ sites were initially in the TMA^+ salt form and TMA^+ was used as the eluant. Ion exchange partition coefficients for the alkylpyridiniums (k^{Py^+}) were calculated from the retention data as follows:

$$k^{\text{Py}^+} = k' V_M / V_S \quad (1)$$

where k' is the capacity factor (15), V_M is the mobile phase volume, and V_S is the stationary phase volume. The capacity factors were determined from the peak maxima. The ion exchange selectivity coefficient ($K_{\text{TMA}^+}^{\text{Py}^+}$) for the exchange of TMA^+ with an alkylpyridinium (Py^+ , i.e., the reaction)



is given by:

$$K_{\text{TMA}^+}^{\text{Py}^+} = [\text{Py}^+]_{(\text{Film})} [\text{TMA}^+]_{(\text{Aq})} / [\text{Py}^+]_{(\text{Aq})} [\text{TMA}^+]_{(\text{Film})} \quad (3)$$

Equation (1) may be substituted into equation (3) to give,

$$K_{TMA}^{Py^+} = k^{Py^+} [TMA^+]_{(Aq)} / [TMA^+]_{(Film)} \quad (4)$$

Because the concentration of TMA^+ in the aqueous phase was high (1 M), it was assumed to be constant (16). Furthermore, by injecting small quantities of the alkylpyridiniums, the average number of sites occupied by an alkylpyridinium can be kept negligibly small (16) making $[TMA^+]_{(Film)}$ just the capacity of the column divided by V_S . These considerations simplify calculations of $K_{TMA}^{Py^+}$ (equation (4)). All ODS-Nafion columns prepared showed analogous retention characteristics. The results presented here were obtained on a single column which contained 2.6 moles of $-SO_3^-$ sites, $V_S = 1.8 \mu L$, $V_M = 1.6 mL$. The selectivity coefficients showed no significant variation with concentration of the alkylpyridinium when alkylpyridinium concentration varied over the range 5×10^{-5} to 5×10^{-4} M. A gradual decrease in K was observed at concentrations higher than ca. 10^{-3} M.

Extremely long retention volumes were obtained when aqueous solutions of inorganic salts were used as the eluants for the alkylpyridiniums. Because of excessive band broadening, detection of such highly retained solutes proved difficult. For this reason, we adopted a convention of waiting 35 min. for a band to elute. If no peak was detected after this time interval, the experiment was terminated and the solute was flushed from the column with a solution of NaBr in methanol.

Efficiencies of both the ODS and ODS-Nafion columns were evaluated by determining numbers of theoretical plates (17) and asymmetry factors (18). Phenol, eluted with 50:50 methanol-water and propylpyridinium eluted with aqueous 1 M TMABr were used to evaluate plate numbers for the ODS and ODS-Nafion columns, respectively. Ethylpyridinium eluted with 0.95 M TMABr

was used to determine the asymmetry factors.

RESULTS AND DISCUSSION

General Retention Characteristics of ODS-Nafion. If partition or ion exchange selectivity coefficients are to be calculated from retention data, the void volume, V_M , must first be measured. While an accurate determination of V_M is never a trivial matter (14), because Nafion has both reversed phase and ion exchange characteristics, measuring V_M for Nafion-based columns is particularly difficult. Obviously, cations and molecules which can engage in hydrophobic interactions with Nafion will produce spuriously large V_M values. Furthermore, if an anion is used to determine V_M , low values could be obtained due to electrostatic exclusion of the anion from portions of the mobile phase. We have observed this co-ion exclusion effect when eluting low concentrations of p-toluenesulfonate from the Nafion-based columns (vide infra).

It is important to note that co-ion exclusion decreases and eventually becomes negligible as the concentration of the co-ion in the mobile phase increases (19). Because a small inorganic anion at high concentrations will have no hydrophobic interaction and no electrostatic interaction (either attractive or repulsive) with Nafion, such an anion seems to be the ideal candidate for determination of V_M for Nafion-based HPLC columns. We have used aqueous NaNO_3 solutions (14) (0.3 to 1.0 M) to determine V_M . No variation in V_M with concentration of NaNO_3 was seen over this high concentration range.

Comparisons of retention volumes, V_R 's, for the alkylpyridiniums on ODS columns with V_R 's on ODS-Nafion clearly showed that the Nafion coating drastically altered the retention characteristics of ODS. For example,

when 100% methanol was used as the eluant, propylpyridinium had a V_R of 3.6 mL on an ODS column and a V_R of greater than 35 mL on the ODS-Nafion column. If, however, 95% methanol-5% 1 M TMABr was used, propylpyridinium was eluted from the ODS-Nafion column in 2.8 mL. Similar results were obtained with the other pyridiniums. Because the pyridiniums would not elute from the ODS-Nafion column (in under 35 min.) unless salt was added to the mobile phase, these studies strongly suggested that ODS-Nafion was, as expected, acting as a cation exchange material. This conclusion is supported by the fact that both anions and neutrals could be easily eluted from ODS-Nafion columns with pure methanol. For example, V_R 's for benzene and p-toluenesulfonate (PTS) are 2.3 and 1.4 mL, respectively. Note that V_R for PTS is less than the measured V_M (1.6 mL). As noted above, this is undoubtedly due to exclusion of this anion from portions of the mobile phase.

The importance of hydrophobic interactions became apparent during attempts to elute the pyridiniums with 100% aqueous mobile phases. Salts containing inorganic cations (e.g., Na^+ , K^+) would not elute the larger pyridiniums from the ODS-Nafion column (in under 35 min.), while salts containing organic cations (e.g., TMA^+ , tetraethylammonium) would. For example, V_R for propylpyridinium using aqueous 0.1 M TMABr as the eluant was 5.1 mL while V_R using aqueous 0.1 M NaBr was greater than 35 mL. In general, with aqueous mobile phases, only an organic cation could elute an organic cation from the ODS-Nafion column. In contrast, in pure methanol mobile phases, nearly any cation (e.g., Na^+ , K^+ , TMA^+) could elute the pyridiniums. (For example, V_R for ethylpyridinium was 4.5 mL when methanolic 0.1 M KBr was used as the eluant). These observations corroborate prior conclusions (1,3-6) regarding the importance of hydrophobic interactions to counterion binding in Nafion (vide infra).

The preceding studies indicated that Nafion on ODS displayed solubility and ion exchange properties similar to bulk Nafion membranes (4) and to ca. 1 to 2 μM thick Nafion films on electrode surfaces (1). This is an important observation because despite its speed and convenience, this HPLC procedure would be of little value if data obtained were not representative of the inherent properties of the polymer being studied. To further test the fidelity of the method, ion exchange selectivity coefficients for the replacement of Na^+ with MV^{2+} , i.e. $K_{\text{Na}^+}^{\text{MV}^{2+}}$, were determined. In our electrochemical isotherm study (1), ion exchange selectivity coefficients were reported in terms of mole fractions rather than concentrations of ions in the polymer phase. Converting the value of $K_{\text{Na}^+}^{\text{MV}^{2+}}$ obtained (1) to the corresponding concentration-based value produces $K_{\text{Na}^+}^{\text{MV}^{2+}} = 4.0 (\pm 0.2) \times 10^3$. With the HPLC procedure the value of $K_{\text{Na}^+}^{\text{MV}^{2+}}$ obtained varied with the molarity of (aqueous) NaBr used as the eluent decreasing from $4.64 (\pm 0.05) \times 10^3$ (2 M NaBr) to $1.97 (\pm 0.05) \times 10^3$ (1 M NaBr). This variation in $K_{\text{Na}^+}^{\text{MV}^{2+}}$ with ionic strength is not surprising since these are selectivity coefficients (equation 3) and not thermodynamic selectivity constants (20,21). The agreement between the two methods is excellent.

Ion Exchange Selectivity Coefficients. Aqueous ion exchange selectivity coefficients (vs. TMA^+) for the various alkylpyridinium ions are shown in Table 1. It is first important to note the immense sizes of these selectivity coefficients. Yeager and Steck (22) obtained ion exchange selectivity coefficients for various monovalent, inorganic ions in Nafion membranes; the largest selectivity coefficient observed was $K_{\text{H}^+}^{\text{Cs}^+}$ which had a value of 9.1 (22). The selectivity coefficients for the hydrophobic ions studied here are from 2 to 3 orders of magnitude larger than this.

Furthermore, the selectivity coefficients shown in Table I are measured vs. TMA^+ whereas Yeager's (22) are measured vs. H^+ . Because inorganic ions will not even elute the larger pyridiniums from the Nafion column (in under 35 min.), values of $K_{\text{H}^+}^{\text{Py}^+}$, if they could be directly measured, would be even larger than the values (vs. TMA^+) reported here. These data are very clear evidence that Nafion shows tremendous preference for hydrophobic cations relative to simple inorganic cations (1).

The role of hydrophobic interactions in the binding of counterions to Nafion is more dramatically demonstrated, and placed on more quantitative terms, through a plot of $\log K_{\text{TMA}^+}^{\text{Py}^+}$ vs. number of carbon atoms in the pyridinium. This "free energy plot" (23) is linear (slope = 0.380, correlation coefficient = 0.996), demonstrating that each increment of molecular bulk (i.e., hydrophobicity) adds an increment of thermodynamic driving force to the ion exchange reaction. From the slope of this line, it can be calculated that each additional carbon contributes an additional -0.518 kcal/mole to the standard free energy change for the ion exchange reaction of an alkylpyridinium.

As noted by Rothbart (24), equation 4 can be rearranged as follows

$$\log k^{\text{Py}^+} = \log[\text{TMA}^+]_{(\text{Film})} + \log K_{\text{TMA}^+}^{\text{Py}^+} - \log[\text{TMA}^+]_{(\text{Aq})} \quad (5)$$

If, over a given eluent concentration range, the ion exchange selectivity coefficient is constant, a plot of $\log k^{\text{Py}^+}$ vs. $-\log[\text{eluent}]$ is linear and the slope is equal to the charge on the exchanging ion (24). Such a plot can be used to confirm that an ion exchange reaction is, indeed, occurring and to assess the stoichiometry of this reaction (24). As noted above, ion exchange selectivity coefficients for the Nafion-based columns are not constant over the eluent concentration ranges which produce manageable

retention volumes. The nonconstancy of k_{TMA}^{Py+} is illustrated by the data in Table II. A plot of $\log k^{Py+}$ vs. $-\log[\text{eluent}]$ is of little value for this system.

Equation (5) may be rearranged as follows

$$\log k^{Py+} = \log [TMA^+]_{(Film)} + \log \frac{k_{TMA}^{Py+}}{[TMA^+]_{Aq}} \quad (6)$$

Thus, a plot of $\log k^{Py+}$ vs. $\log(k_{TMA}^{Py+}/[TMA^+]_{Aq})$ should be linear with a slope of 1.0. Such a plot is analogous to Rothbart's (24) (equation (5)) but compensates for the variation in k_{TMA}^{Py+} with $[TMA^+]_{Aq}$. When the data in Table II are plotted according to equation (6), a line (correlation coefficient = 0.9996, intercept = 0.224) with a slope of 0.98 is obtained. The close agreement between the predicted and experimental slopes confirms that the Nafion-based columns are acting as cation exchange materials.

Efficiency and Resolution. Figure 1 shows a typical chromatogram for a mixture of three of the alkylpyridinium ions on an ODS-Nafion column. Note that these pyridiniums differ in molecular weight by only one methylene group yet good separation is obtained. These data suggest that Nafion-based HPLC columns should be useful for separations of organic cations. Indeed, Kirkland (11,12) has demonstrated that a number of separations of practical interest can be performed on HPLC columns prepared from a low EW version of Nafion. It is important to note that these low EW Nafion films are soluble in ethanol and other organic solvents whereas high EW Nafion films can be made insoluble (25) in all solvents (at temperatures below ca. 200°C). Therefore, HPLC columns prepared from high EW Nafion have the advantage of being usable in any desired solvent system. Furthermore, a comparison (1) of ion exchange data for low (2) and high (1) EW Nafion suggests that low EW Nafion has

a much lower affinity for hydrophobic cations.

Pronounced peak tailing is observed in the chromatogram shown in Figure 1. Asymmetry factors of about 11 were typically obtained on ODS-Nafion whereas asymmetry factors of about 6 were obtained on our homepacked ODS columns. The poorer symmetry observed with the ODS-Nafion columns could be caused by either thermodynamic (i.e., non-linear isotherm), diffusive or kinetic problems. Our studies of ion exchange in Nafion-based chemically modified electrodes have shown that the partition isotherm for an organic cation begins to bend over when about 1% of the available $-SO_3^-$ sites in the Nafion film are occupied by this cation (1). For this reason, our initial assumption was that the peak tailing was the result of isotherm non-linearity. However, peak tailing is observed under conditions where calculations (15) show that less than 0.001% of the $-SO_3^-$ sites are occupied by the alkylpyridiniums (i.e., very low sample concentrations). Therefore, the enhanced asymmetry for the ODS-Nafion columns appears to be dynamic in origin. We are currently studying the effects of the solvent and the film thickness on the column dynamics.

A plot of height equivalent to a theoretical plate (HETP) vs. flow rate for an ODS-Nafion column is shown in Figure 2. The typical (26) increase in HETP with flow rate is observed. However, as was also observed by Kirkland (11) for columns prepared from the low EW Nafion, the HETP curve exhibits a pronounced flattening at higher flow rates. This means that higher flow rates may be used without significant loss of efficiency (11).

CONCLUSIONS

These studies have shown that an HPLC procedure can be used as a convenient and rapid tool for studying ion exchange reactions in ionomers. The ion exchange data obtained have been shown to be the same (both

qualitatively and quantitatively) as data obtained from a tedious and time consuming isotherm method (1). The isotherm data were obtained from Nafion films ranging from 1 to 2 μM in thickness which had up to 40% of their $-\text{SO}_3^-$ sites occupied by the exchanging ion. Clearly, the ion exchange selectivity coefficients in this case describe bulk film rather than surface processes (1). In contrast, in the current study the loading of the exchanging ion was kept below 1% of the available $-\text{SO}_3^-$ sites and, while the film thicknesses are unknown, the rather low capacities of these columns suggest that these films are very thin. These are interesting points because they suggest that the ion exchange data in the HPLC experiment might reflect surface rather than bulk processes; future studies will assess how well ion exchange data for columns like those described here conform to current theories (27) of surface ion exchange processes. If the data obtained here do reflect surface rather than bulk film ion exchange, the thermodynamics of these processes must be very similar.

The results obtained corroborate earlier conclusions regarding the importance of hydrophobic interactions to counterion binding in Nafion (1,3-6). Conventional ion exchange resins do not show Nafion's remarkable affinity for hydrophobic counterions (1,28). For example, Gregor and Bregman studied ion exchange reactions of a variety of alkyl and phenyl-alkylammonium ions in sulfonated polystyrene resins (28); these resins contained from about 1 to 35% cross-linking. While selectivity coefficients as large as about 20 were observed (28), none of the resins studied produced selectivity coefficients as large as those shown in Table 1 or reported in our previous publication (1). We are currently using the HPLC method in studies aimed at ascertaining why Nafion's ion exchange characteristics are so unusual.

REFERENCES

1. Szentirmay, M. N.; Martin, C. R. Anal. Chem., In Press.
2. White, H. S.; Leddy, J.; Bard, A. J. J. Am. Chem. Soc. 1982, 104, 4811.
3. Martin, C. R.; Rubinstein, I.; Bard, A. J. J. Am. Chem. Soc. 1982, 104, 4817.
4. Martin, C. R.; Freiser, H. Anal. Chem. 1981, 53, 902.
5. Martin, C. R.; Dollard, K. A. J. Electroanal. Chem. 1983, 159, 127.
6. Prieto, N. E.; Martin, C. R. J. Electrochem. Soc. 1984, 131, 751.
7. Schneider, J. R.; Murray, R. W. Anal. Chem. 1982, 54, 1508.
8. Szentirmay, M. N.; Martin, C. R. J. Electrochem. Soc. 1984, 131, 1652.
9. Martin, C. R.; Rhoades, T. A.; Ferguson, J. A. Anal. Chem. 1982, 54, 1639.
10. Prieto, N. E.; Martin, C. R. Unpublished results, Texas A&M University, November, 1983.
11. Kirkland, J. J. J. Chromatogr. Sci. 1969, 7, 361.
12. Kirkland, J. J. J. Chromatogr. Sci. 1970, 8, 72.
13. Snyder, L. R.; Kirkland, J. J. Introduction to Modern Liquid Chromatography, 2nd Ed., John Wiley and Sons, Inc., NY, 1979, p. 211.
14. Wells, M. J. M.; Clark, C. R. Anal. Chem. 1981, 53, 1341.
15. Karger, B. L.; Snyder, L. R.; Horvath, C. An Introduction to Separation Science, John Wiley and Sons, NY, 1973, pp. 30,31.
16. Fietelson, J.; in Marinsky, J. A., Ed. Ion Exchange, Marcel Dekker, Inc. NY, 1969, Vol. 2, Chap. 4.
17. Snyder, L. R.; Kirkland, J. J. Introduction to Modern Liquid Chromatography, 2nd Ed., John Wiley and Sons, Inc., NY, 1979, p. 28.
18. Snyder, L. R.; Kirkland, J. J. Introduction to Modern Liquid Chromatography, 2nd Ed., John Wiley and Sons, Inc., NY, 1979, p. 222.
19. Diamond, R. M.; Whitney, D. C., in, Marinsky, J. A., Ed., Ion Exchange, Marcel Dekker, Inc., NY, 1966, Vol. 1, pp. 284-286.
20. Laitinen, H. A.; Harris, W. E. Chemical Analysis, 2nd Ed., McGraw-Hill, NY, 1979, p. 18.
21. Laitinen, H. A.; Harris, W. E. Chemical Analysis, 2nd Ed., McGraw-Hill, NY, 1979, p. 16.

22. Yeager, H. L.; Steck, A. Anal. Chem. 1979, 51, 862.
23. Marinsky, J. A.; Marcus, Y. Ion Exchange and Solvent Extraction, Vol. 6, Marcel Dekker, NY, 1974, p. 5.
24. Rothbart, H. L., in, Karger, B. L.; Snyder, L. R.; Horvath, C., Eds., An Introduction to Separation Science, John Wiley and Sons, NY, 1973, pp. 354,355.
25. Moore, R. B. III; Kellman, R.; Martin, C. R., In prep.
26. Karger, B. L.; Snyder, L. R.; Horvath, C. An Introduction to Separation Science, John Wiley and Sons, NY, 1973, p. 279.
27. Afrashtehfar, S.; Cantwell, F. F. Anal. Chem. 1982, 54, 2422.
28. Gregor, H. P.; Bregman, J. I. J. Colloid. Sci. 1951, 6, 323.

Credit

This work was supported in part by the Office of Naval Research.

Acknowledgement

The author's are pleased to acknowledge valuable discussions with
M. F. Burke.

Table I. Ion exchange selectivity coefficients on ODS-Nafion column.^a

Pyridinium Ion	$K_{TMA^+}^{Py^+}$
Ethylpyridinium	4.3×10^2
Propylpyridinium	8.5×10^2
Butylpyridinium	2.1×10^3
Pentylpyridinium	5.7×10^3

^aMobile phase = 0.95 M aqueous TMABr, flow rate = 1 mL/min, 10 μ L samples of 10^{-3} M aqueous pyridinium solution injected.

Table II. Dependence of $K_{TMA^+}^{Py^+}$, for ethylpyridinium, on concentration of TMA^+ for the Nafion-based columns.

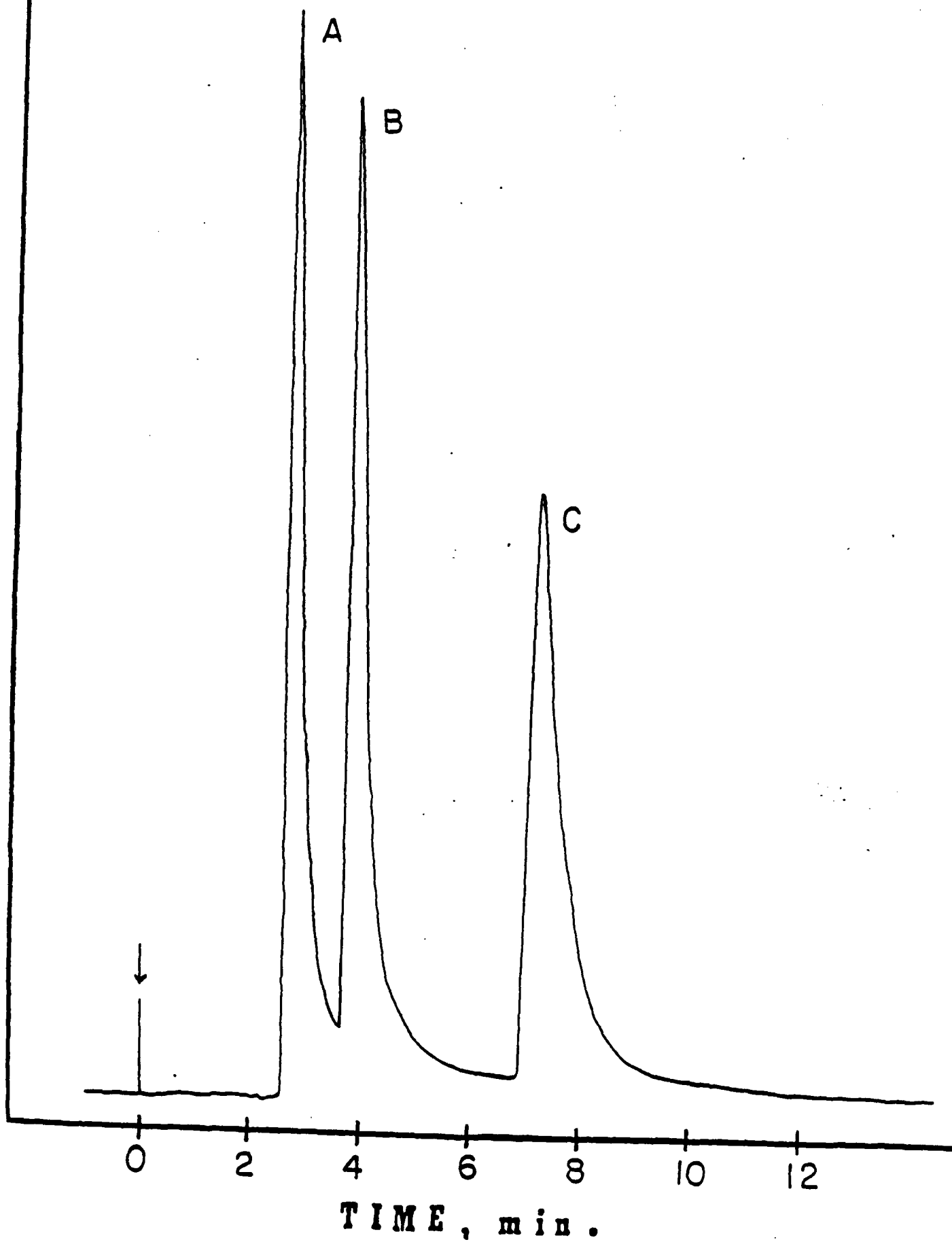
$[TMA^+]$	k^{Py^+}	$K_{TMA^+}^{Py^+}$
0.1	1.88×10^3	131
0.2	1.37×10^3	191
0.3	1.14×10^3	239
0.4	1.03×10^3	286
0.5	9.29×10^2	323
0.6	8.38×10^2	350
0.8	7.30×10^2	406

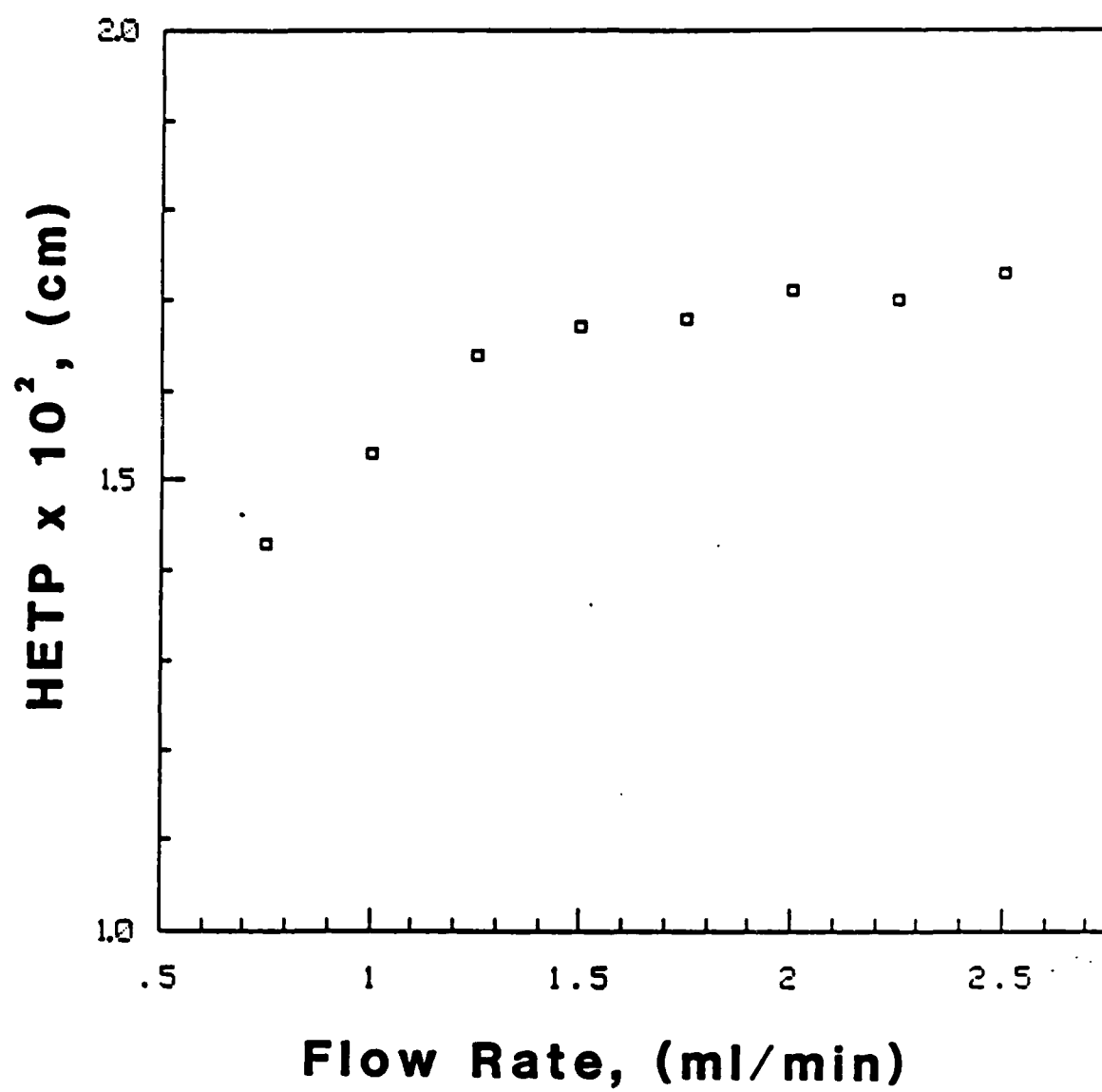
Figure Captions

Figure 1. Chromatogram for a mixture of A, ethylpyridinium; B, propylpyridinium; C, butylpyridinium on ODS-Nafion. All constituents 10^{-3} M (aqueous). Eluant is 1.0 M TMABr aqueous. Flow rate = 1 mL min^{-1} .

Figure 2. Plot of HETP vs. flow rate for an ODS-Nafion column. Solute is propylpyridinium. Eluant is 0.95 M TMABr.

ABSORBANCE





TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Office of Naval Research
Attn: Code 413
800 North Quincy Street
Arlington, Virginia 22217

2

ONR Pasadena Detachment
Attn: Dr. R. J. Marcus
1030 East Green Street
Pasadena, California 91106

1

Commander, Naval Air Systems Command
Attn: Code 310C (H. Rosenwasser)
Department of the Navy
Washington, D.C. 20360

1

Defense Technical Information Center
Building 5, Cameron Station
Alexandria, Virginia 22314

12

Dr. Fred Saalfeld
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375

1

U.S. Army Research Office
Attn: CRD-AA-IP
P. O. Box 12211
Research Triangle Park, N.C. 27709

1

Mr. Vincent Schaper
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

Naval Ocean Systems Center
Attn: Dr. S. Yamamoto
Marine Sciences Division
San Diego, California 91232

1

Naval Ocean Systems Center
Attn: Mr. Joe McCartney
San Diego, California 92152

Naval Weapons Center
Attn: Dr. A. B. Amster,
Chemistry Division
China Lake, California 93555

Naval Civil Engineering Laboratory
Attn: Dr. R. W. Drisko
Port Hueneme, California 93401

Dean William Tolles
Naval Postgraduate School
Monterey, California 93940

Scientific Advisor
Commandant of the Marine Corps
(Code RD-1)
Washington, D.C. 20380

Naval Ship Research and Development
Center
Attn: Dr. G. Bosmajian, Applied
Chemistry Division
Annapolis, Maryland 21401

Mr. John Boyle
Materials Branch
Naval Ship Engineering Center
Philadelphia, Pennsylvania 19112

Mr. A. M. Anzalone
Administrative Librarian
PLASTEC/ARRADCOM
Bldg 3401
Dover, New Jersey 07801

Dr. Jerry J. Smith
Chemistry Division
Office of Naval Research
Department of the Navy
Arlington, Virginia 22217

1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>	<u>Co</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SOO 5NH United Kingdom
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	1	Dr. Sam Perone Chemistry & Materials Science Department Laurence Livermore National Lab. Livermore, California 94550
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research and Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Johnson Controls 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201
Dr. T. Katan Lockheed Missiles and Space Co., Inc. P. O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attn: Technical Library 2485 Charleston Road Mountain View, California 94040
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1	

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139		Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
S. Ruby DOE (STOR) 600 E Street Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. Bernard Spielvogel U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	Dr. Denton Elliott Air Force Office of Scientific Research Bolling AFB Washington, D.C. 20332	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. David Aikens Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. A. P. B. Lever Chemistry Department York University Downsview, Ontario M3J1P3 Canada	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England		Dr. Stanislaw Szpak Naval Ocean Systems Center Code 6343 San Diego, California 95152	1
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362		Dr. Gregory Farrington Department of Materials Science and Engineering University of Pennsylvania Philadelphia, Pennsylvania 19104	1
Dr. John Kincaid Kaman Sciences Corporation 1911 Jefferson Davis Hwy., Suite 1200 Arlington, Virginia 22202		Dr. Bruce Dunn Department of Engineering & Applied Science University of California Los Angeles, California 90024	

TECHNICAL REPORT DISTRIBUTION LIST, 359

No.
Copies

Co

M. L. Robertson Manager, Electrochemical and Power Sonics Division Naval Weapons Support Center Crane, Indiana 47522	1	Dr. T. Marks Department of Chemistry Northwestern University Evanston, Illinois 60201
Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1	Dr. D. Cipris Allied Corporation P. O. Box 3000R Morristown, New Jersey 07960
Dr. Micha Tomkiewicz Department of Physics Brooklyn College Brooklyn, New York 11210	1	Dr. M. Philpot IBM Corporation 5600 Cottle Road San Jose, California 95193
Dr. Lesser Blum Department of Physics University of Puerto Rico Rio Piedras, Puerto Rico 00931	1	Dr. Donald Sandstrom Washington State University Department of Physics Pullman, Washington 99164
Dr. Joseph Gordon, II IBM Corporation K33/281 5600 Cottle Road San Jose, California 95193	1	Dr. Carl Kannewurf Northwestern University Department of Electrical Engineering and Computer Science Evanston, Illinois 60201
Dr. Robert Somoano Jet Propulsion Laboratory California Institute of Technology Pasadena, California 91103	1	Dr. Edward Fletcher University of Minnesota Department of Mechanical Engineering Minneapolis, Minnesota 55455
Dr. Johann A. Joebstl USA Mobility Equipment R&D Command DRDME-EC Fort Belvoir, Virginia 22060	1	Dr. John Fontanella U.S. Naval Academy Department of Physics Annapolis, Maryland 21402
Dr. Judith H. Ambrus NASA Headquarters M.S. RTS-6 Washington, D.C. 20546	1	Dr. Martha Greenblatt Rutgers University Department of Chemistry New Brunswick, New Jersey 08903
Dr. Albert R. Landgrebe U.S. Department of Energy M.S. 6B025 Forrestal Building Washington, D.C. 20595	1	Dr. John Wassib Kings Mountain Specialties P. O. Box 1173 Kings Mountain, North Carolina 28086

TECHNICAL REPORT DISTRIBUTION LIST, 359No.
CopiesN
Cor

Dr. J. J. Brophy University of Utah Department of Physics Salt Lake City, Utah 84112	1
Dr. Walter Roth Department of Physics State University of New York Albany, New York 12222	1
Dr. Thomas Davis National Bureau of Standards Polymer Science and Standards Division Washington, D.C. 20234	1
Dr. Charles Martin Department of Chemistry Texas A&M University	1
Dr. Anthony Samuels Institute of Gas Technology 3424 South State Street Chicago, Illinois 60616	1
Dr. H. Tachikawa Department of Chemistry Jackson State University Jackson, Mississippi 39217	1
Dr. W. M. Risen Department of Chemistry Brown University Providence, Rhode Island	1

END

FILMED

9-84